

BENZOTRIAZOLE COMPOUND AND HOMOPOLYMER OR COPOLYMERS THEREOF

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the preparation and use of benzotriazole compounds. More particularly, it relates to benzotriazole compounds having vinyl groups which can act as monomers for homo- and copolymerization. It also relates to homopolymer or copolymers of benzotriazole compounds having vinyl groups. The most effective application of these materials are for ultraviolet protection of plastics, wood and other organic materials.

2. Description of the Prior Arts

The subject matter of the present application is related to the subject matter of copending application Ser. No. 238,090 filed Feb. 25, 1981.

Plastics used in outdoor are exposed to deleterious solar radiation of a wavelength of 290-400 nm (mμ). The polymer chain or functional group of the polymer exposed to solar radiation absorbs ultraviolet radiation and is excited to a higher energy level, and there is the possibility that certain photochemical reactions are caused. The photochemical reaction could cause degradation of a polymer chain or formation of crosslinkage or introduction of functional groups in to the plastic material. An ultraviolet absorber is usually incorporated into the plastic material in order to protect it from degradation caused by solar radiation. Ultraviolet absorbers absorb most or all of the harmful radiation and emit them as harmless radiation and also absorbing photoexcited energy in the polymer and emit it as harmless energy, which is necessary for stabilizing polymers. Ultraviolet absorbers should be effective for a long time, it is preferable that the ultraviolet absorber does not cause deterioration or discoloration of the plastic material or should not be leached out in contact with a solvent or the other lower molecular weight material. The peak absorption of the ultraviolet absorber should be in the most sensitive wavelength at which the polymer is used. The optimum effect as ultraviolet absorber for protecting plastic materials from harmful effect of solar radiation should be considered from the point of view of photochemical properties and other functions. For example, it is not enough to have only high absorbancy index (extinction coefficient) in an ultraviolet region and nondestructive emission of absorbed energy. In general, the most important factor for the selection of ultraviolet absorbers is not only the photochemical property. It is necessary for the ultraviolet absorber to have the desired photochemical properties, for example, to have high absorbancy index in the wavelength region of 300-350 nm. The ultraviolet absorber should be stable and not color or decompose on exposure solar radiation. In order to be not colored the ultraviolet absorber preferably has low absorbancy in the long wavelength region. If the ultraviolet absorber should be considered for preventing sun-burn it should be effective for a long time. The cosmetic ultraviolet absorbers should have low toxicity without any allergic effect. Moreover, the tissue toxicity in penetration into skin should be also low. For example, low molecular compounds such as β-aminobenzoic acid derivatives and salicylic acid derivatives are not satisfactory. The effect of polymeric ultraviolet absorbers depends upon the molecular weight and its volatility. Polymeric ultraviolet

let absorbers having low volatility and low leachability is preferable. In 2-hydroxy-4-alkoxybenzophenones, this has been attempted but not achieved satisfactorily by having a long alkoxy group, which also improves the compatibility with the polymer. Especially with hydrocarbon polymers compatibility is increased and volatility is decreased by the increase of the length of side chain groups, for example, to the length of the dodecyloxy group.

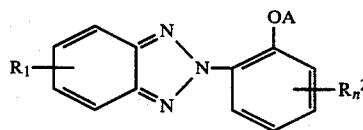
Polymeric ultraviolet absorbers have been known in prior arts. 2-Hydroxy-4-methacryloxybenzophenone is obtained by reacting 2,4-dihydroxybenzophenone with methacrylic acid derivatives. Other derivatives have been obtained from 2,4-dihydroxybenzophenone. For example, the allyl ether of 2,2',4-trihydroxybenzophenone and 4-chloromethylstyrene. Allyloxy, acrylamino, methacrylamino, vinylsulfoxy and vinyloxy derivatives of 2-(2-hydroxy-5-phenyl)benzotriazole have also been described and their copolymerization with such a comonomer as styrene, acrylonitrile or butadiene are claimed.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide benzotriazole compounds as a source for polymeric ultraviolet absorbers especially 2-hydroxy benzotriazole compounds having a polymerizable unsaturated group on the phenyl ring of the benzotriazole group, and the intermediates thereof.

Another object of the present invention is to provide 2-hydroxyphenyl benzotriazole compounds having a polymerizable unsaturated groups on the phenyl ring of the benzotriazole group which can be homopolymerized or copolymerized with a comonomer to obtain polymeric ultraviolet absorbers.

The benzotriazole compounds of the present invention have the following formula



wherein A represents a hydrogen atom, or a acetyl group; R¹ represents a vinyl or haloethyl group or ethyl group; R² represents a C₁₋₄ alkyl group and n is 1 or 2, R₂² need not be the same group in a formula.

In the formula, R¹ is preferably at the 5-position, but may be at 4-position. Among the compounds the most effective compounds have a vinyl group as the R₁ group. The compounds having ethyl or haloethyl group as R¹ are effective as the intermediate for the synthesis of compounds having a vinyl groups as R¹. The haloethyl group is preferably the 1-haloethyl having Cl, Br or I especially Br as the halogen atom.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the present invention, the most effective compounds as the source for polymeric ultraviolet absorbers useful for a number of applications are 2(2-hydroxy-5-methylphenyl)-5-vinyl-2H-benzotriazole, and 2(2-acetoxy-5-methylphenyl)-5-vinyl-2H-benzotriazole.

The characteristics of the compounds of the present invention are excellent optical properties with a broad absorption having the highest intensity in ultraviolet